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(54) Depositing silicon on metal

(57) To protect a metal surface, there is deposited thereon a non-oxidised silicon coating having a thickness of at least 0.25 microns, the silicon coating being applied by chemical vapour deposition in a single step treatment from a mixture of monosilane and an inert gas or from a mixture of monosilane hydrogen and an inert gas, at a temperature in excess of 748K and at substantially atmospheric pressure. The thickness is usually substantially greater than 0.25 microns, typically being at least 0.7 microns but may be substantially thicker than this.

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SPECIFICATION

Methods of protecting a metal surface

This invention relates to methods for protecting a metal surface using a silicon coating.

It is known to protect a metal surface by putting a silicon coating thereon. Heretofore however it has been considered desirable to oxidise any such silicon coating or to deposit silica directly on the metal for corrosion protection. Patent Specification No. 1463053 describes a technique in which a glassy silica coating is desposited on a metal using a gas-phase reaction of monosilane (SiH_4) with oxygen and, in Specification No. 1511353, a coating technique using diborane in addition to monosilane and oxygen is described. With such techniques however problems arise with dust formation, particularly siloxane dust. To avoid the dust problem, a technique is described in Specification No. 1530337 in which a thin silicon coating is deposited on a metal surface and is subsequently oxidised at a high temperature under carefully controlled oxidation potential conditions such that the oxidation of the silicon is faster than that of the substrate. This technique however is complex and there are problems in evenly coating complex objects, such as for example arrays of boiler tubes, with the required thin coating of silicon.

According to the present invention a method of protecting a metal surface comprises the step of depositing thereon a non-oxidised silicon coating having a thickness of at least 0.25 microns, the silicon coating being applied by chemical vapour deposition in a single step treatment from a mixture of monosilane (SiH_4) and an inert gas or a mixture of monosilane, hydrogen and an inert gas at a temperature in excess of 748 K and at substantially atmospheric pressure.

The silicon film, which for most purposes would be at least 0.75 microns thick, and might typically be much thicker is far thicker than has heretofore been proposed for protective coatings for metals. For many corrosion applications, a thickness of 5 microns might be used but, where excessive corrosion rates occur or where erosion is possible, a thickness of up to say 50 microns might be used. With this thick silicon film deposited by the above-mentioned process in a single layer, it has been found possible to avoid any oxidising of the silicon in the coating and hence to obtain a protective layer which protects the underlying substrate. A deposition temperature in excess of 748 K is employed in order to achieve an adequate rate of deposition. Faster deposition can be obtained with higher temperatures and typically a temperature of 773 K might be employed. Maximum temperatures are limited by interdiffusion of silicon with components of the substrate, and for a steel, would depend on the type of steel being protected. With typical ferritic steels with chromium compositions in the range 0—12% and austenitic steels with chromium contents up to 20%, this upper limit will not be below 1300 K. At temperatures in excess of 748 K, the effects of residual oxide films on the metal are eliminated and it is possible to produce the required thick silicon layer in a reasonable time, for example a layer 0.75 microns thick might typically be produced in 24 hours at a temperature of 773 K. The protection is not dependent in any way on the formation of a continuous glassy layer impervious to gas such as has heretofore been considered necessary. The above process enables a uniform layer of silicon, free of silica as a particulate impurity, to be achieved. Freedom from silica particles is desirable as these might disrupt the homogeneity of the layer and leave easy diffusion paths for corrosive gases to the metal surface. By eliminating all particulate material from the silicon layer the risk of spalling of the coating caused by differential thermal expansion of the foreign particles is eliminated.

The process described above may readily be applied for example to boiler sections and associated components immediately after manufacture; conveniently the coating is effected before installation of the components and may readily be associated with other treatment such as solution treatment, tempering and stress-relieving stages of manufacture, all of which are carried out at high temperatures in an inert gas atmosphere. However the process of the present invention may be used directly on installed equipment such as installed boilers by feeding the gases at the required temperature over the surfaces to be protected.

The temperature for carrying out the process is at or above 748 K. In general, the temperature will be kept as close to this value as possible. The maximum temperature would usually be determined by the substrate.

The following is a description of one example of the invention.

A chromium steel element containing 9% chromium by weight, which simulated part of a large boiler, was placed in a closed silica vessel, the lower part of which extended downwardly into a furnace for heating the element. Thermocouples were provided for monitoring the temperature. After putting the specimen in the vessel the vessel was purged with 2% hydrogen in dry argon for 2 to 3 hours and the specimen was then lowered into the hot temperature zone of the furnace to remove the bulk of adsorbed water from the specimen and specimen carrier. The mixture of hydrogen and argon at atmospheric pressure continued to be passed through the vessel with the specimen maintained at the required treatment temperature, typically 773 K. When the water vapour content of the gas leaving the vessel was reduced to less than 100 vpm, the gas mixture was changed to 500 vpm monosilane, 2% (by volume) hydrogen, remainder argon. After 24 hours exposure, the gas mixture was changed to 2% (by volume) of hydrogen in argon to remove residual silane.

It was found that elemental silicon was

deposited on the steel element to give a layer about 0.75 microns thick.

Various steels and alloys have been coated by the method described above to produce an elemental silicon outer coating on the test specimens at least 0.75 microns thick and up to 8 microns thick. These test specimens included (a) a binary chromium iron alloy containing 9% Cr 91% Fe by weight (b) a 9% Cr steel, and (c) an English rimming steel, that is a mild steel with no detectable silicon content which is known to be very susceptible to rapid and destructive breakaway corrosion when exposed to carbon dioxide at high temperatures.

The treated article was compared with an untreated article to measure corrosion resistance using an accelerated corrosion testing atmosphere. It was found that a reduction in the oxidation rate by a factor in excess of 30 times was obtained and, in some experiments, considerably larger corrosion benefit factors were achieved.

Claims

1. A method of protecting a metal surface comprising the step of depositing thereof a non-oxidised silicon coating having a thickness of at least 0.25 microns, the silicon coating being applied by chemical vapour deposition in a single step treatment from a mixture of monosilane ($Si H_4$) and an inert gas or a mixture of monosilane, hydrogen and an inert gas at a temperature in excess of 748 K and at substantially atmospheric pressure.

2. A method as claimed in Claim 1 wherein the silicon film is at least 0.75 microns thick.

3. A method as claimed in Claim 2 wherein the silicon layer is deposited by a chemical vapour deposition over a period of substantially 24 hours.

4. A method as claimed in any of the preceding claims wherein the temperature of treatment is in excess of 773 K.

5. A method as claimed in any of the preceding claims wherein the metal surface is heated and exposed to an argon-hydrogen mixture to remove any water or water vapour before being coated with silicon.

6. A method of protecting a metal surface with a layer of silicon substantially as hereinbefore described.

7. A metal surface protected by a silicon coating applied as claimed in any of the preceding claims.

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